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Experimental and theoretical thermodynamic properties of RS-(±)- and S-(+)-mandelic acids

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ABSTRACT

The enthalpies of formation of RS-(±)- and S-(+)-mandelic acids were measured using high-precision combustion calorimetry. Vapor pressures of the acids were measured using the transpiration method. The enthalpies of sublimation of these compounds at 298.15 K were derived from vapor pressure temperature dependencies. Molar enthalpies of the solid state phase transitions were measured by the DSC. Thermodynamic data on mandelic acids available from the published sources were collected and combined with our experimental results. Thermochemical properties of studied compounds were evaluated and tested for internal and external consistency with different approaches. The methods of quantum chemistry and statistical physics were used to calculate thermodynamic functions of compounds in the ideal gas state in temperature range 298.15 K–1500 K.

1. Introduction

Mandelic acid (MA) and its derivatives are widely used in the industrial and pharmaceutical sectors. This compound exists as two optical enantiomers and racemic form, which affect its pharmacological properties [1]. The acid has been known for its anti-aging effects on the skin along with antibacterial action in treating acne and preventing bacterial infections [1–3]. MA has a structure similar to that of widely known antibiotics but having no toxic effects, which makes it useful as urinary antiseptic [4–6]. The acid can serve as a raw material in manufacturing of many useful products due to its special structure [7]. It is an intermediate substance that is used in the production of synthetic rubber and polymers. Environmental and occupational exposures to toxic solvents in making paints, dyes, paint thinners, rubber, adhesives, pharmaceutical products and plastic materials cause harmful and adverse effect on the people [8–10]. Due to the growing concern regarding exposure to these toxic substances in surroundings, biological and environmental monitoring to assess potential health hazards is crucial. The chemicals are metabolized to MA and excreted in urine enabling the acid to serve as a biomarker for the biological monitoring and preventive measures [11,12].

The properties of MA have not been fully studied. The published values for the heat of combustion of RS-(±)-MA and S-(+)-MA have been measured in 1894 [13] and 1963 [14] correspondingly but exhibit inconsistency. There are references for the measured temperature and enthalpy of fusion obtained via differential scanning calorimetry method [15–17], but no consistency is observed among these values.

In this study, enthalpies of formation in the condensed phase and enthalpies of phase transitions (fusion, sublimation) for RS-(±)-MA and S-(+)-MA were determined using combustion calorimetry, differential scanning calorimetry and transpiration techniques. This is the original research measuring enthalpies of sublimation of compounds. Thermodynamic functions of the mandelic acid in the ideal gaseous state were computed in the range of T = 298.15–1500 K using the molecular and spectral data.

2. Materials and methods

2.1. Materials

Commercial samples of acids – RS-(±)-MA (Alfa Aesar, 99%) and S-(+)-MA (Alfa Aesar, 99+%) - were additionally purified by fractional vacuum sublimation (see Table S1). A confirmation of the absence of changes in acid structures along with the final degree of their purity has

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